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Inhibition of corrosion of carbon steel in acidic medium by using innovative Gemini nonionic surfactant based on stearic acid

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ABSTRACT **: Polyethenoxy di-octadecanoate (GS stearate) is Gemini nonionic surfactant synthesized from stearic acid by reaction with poly ethylene glycol to forming ester compound then prepared ester reacted with 1,2 di bromo ethane to form Gemini nonionic surfactant. FT-IR and 1HNMR spectrum studies were used to confirm this. Surface characteristics of prepared compound were discussed such as surface tension, critical micelle concentration (CMC) and Thermo-dynamic properties. The anti-corrosion properties of these novel surfactants were studied and the results showed good anti-corrosion properties..**

KEYWORDS: Gemini surfactants; Surface-characteristics; Anticorrosion Properties; acid medium.

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I. INTRODUCTION

Surfactants have essential role in several applications such as Detergents, Textiles, coating, and corrosion inhibitors [1-3]. Metal deterioration causes a lot of troubles for the industry, exposes companies to huge losses, and poses refers to the environment including pollution [4, 5]. Formation water, which has high concentrations of dissolved salts like chloride and sulphate ions as well as corrosive dissolved gases like carbon dioxide and hydrogen sulphide, is one of the most corrosive environments in manufacturing processes [6, 7].

One of the most widely utilized techniques for reducing metal corrosion is the use of corrosion inhibitors. Nitrogen, Sulphur, and oxygen atoms should be present in molecules that act as acid inhibitors [8, 9]. By creating an adsorption layer on the metal surface, the inhibitor molecules can separate the metal from the corrosive medium. An inhibitor must interact with anodic and cathodic sites processes in order to be effective in displacing water from a portion of the metallic surface [10-12].

Nowadays, Gemini surfactant have been considered a new generation of surfactants, this kind of surfactant have been consisted of two classical surfactant molecules which chemically bonded together by flexible or rigid spacer [13]. Gemini surfactant prevents corrosion by adhering polar groups (hydrophilic heads) to the metal's surface while the non-polar groups (hydrophobic tails) are driven towards the solution [14].

In our work, we synthesized a novel Gemini nonionic surfactant and investigate it as a corrosion inhibitor of carbon steel in 1M HCL using weight loss in addition to it was studied surface active features.

II. MATERIALS AND METHODS

2.1. Materials:

Octadecanoic acids, polyethylene glycol (400), dibromo ethane, and benzene, were bought from Sigma Aldrich and p.tolune sulfonic acid, ethyl alcohol, and potassium hydroxide, respectively, from AL-Nasr Chemical Company. Carbon steel composition 0.38% carbon, 0.035% phosphorus, 0.088% silicon, 0.5% manganese, and the remaining element is iron

Utilized was a corrosion medium (blank solution) made out of water and 1.0 M hydrochloric acid. The carbon-steel specimens for each test were prepared using a variety of emery sheets with diameters ranging from 400 to 2500.

2.2. Experimental methods

2.2.1 Synthesis of novel Gemini non-ionic surfactants

2.2.1.1 Polyethylene glycol mono stearate Synthesis

In the reaction, 0.3 mol of stearic acid is dissolved in toluene and mixed with 0.3 mol of polyethylene glycol (400) [15].

Dean stark contained 1.8 mL of removed water when the reaction was finished after 8 hours of heating the mixture at 180°c.

2.2.1.2 synthesis of New Gemini nonionic surfactants (Polyethenoxy di-octadecanoate (GS stearate):

Using a 2:1 molar ratio of dibromo ethane and polyethylene glycol mono stearate for the synthesis of the Gemini surfactant, Potassium hydroxide (0.5%) served as the catalyst while ethanol served as the solvent. After 15 minutes of stirring, dibromo ethane was added to the mixture, and the reaction was continuously stirred for 36 hours at 110°C. The mixture was washed several times with diethyl ether to eliminate the unreacted substance after the solvent had been evaporated

Polyethenoxy di-octadecanoate (GS stearate) is Pale brown liquid with a high viscosity and a 93% yield. IR spectrum of compound showed that, stretching bands at 2929, and 2861 cm-1 ($\nu_{C\text{-}H}$, fatty chain), 1733 cm-1 ($\nu_{C=O}$ of ester), 1105 cm-1 ($\nu_{C\text{-}O}$ of ether).

1H NMR δ (ppm): 0.82 (t, 6H, 2 [CH3-CH2-]), 1.22 (S, 56H, 2 [(CH2)14-]), 1.59 (m, 4H, 2 [CH2CH2COO]), 2.36 (t, 4H, 2 [CH2-COO]), 3.59 (s, 68H, 17 [CH2-CH2-O]), 3.67 (t, 4H, 2 [COO-CH2-CH2-O-]), 4.26(t, 4H, 2 [COO-CH2-CH2-O-]).

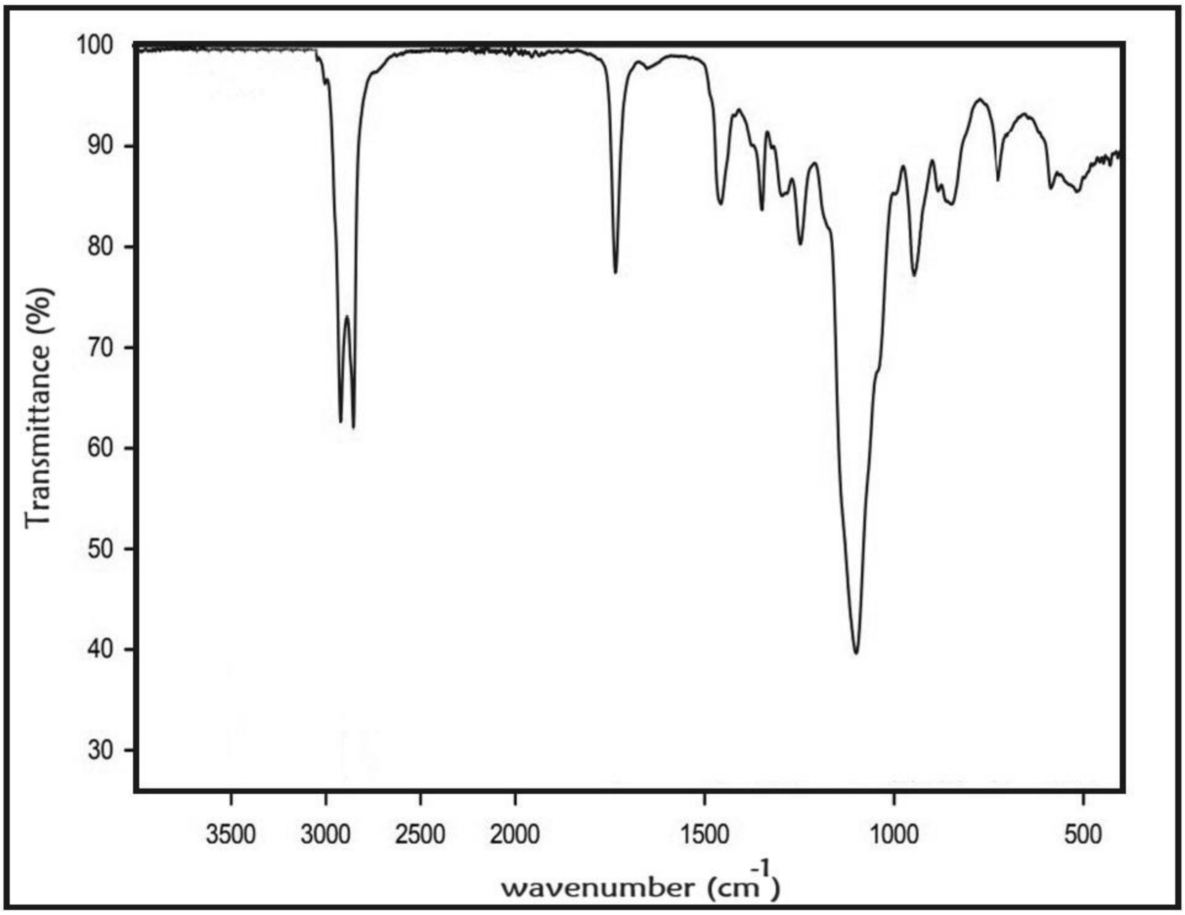

Figure 1: IR spectra of GS stearate.

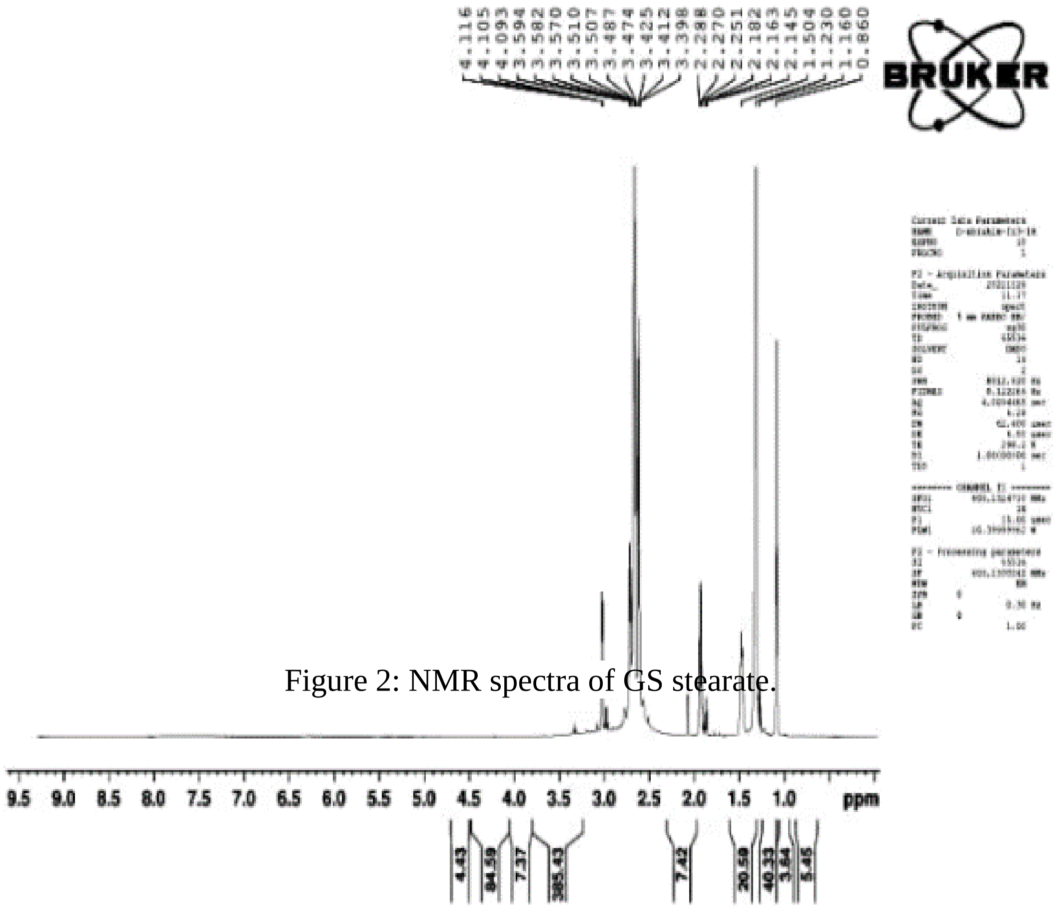

Figure 2: NMR spectra of GS stearate.

2.2.2 Surface properties:

Surface tension:

Tensiometer-K6 processor (Krüss Company, Germany) was used for determining the surface tension values of synthetic surfactants using the ring method. For each experiment, the surface tension of distilled water was principally measured in order to calibrate the instruments and establish the purity value of the water. To eliminate surfactant residues in between measurement runs, the ring was first cleaned with distilled water and then with acetone [16].

Critical micelle concentration (CMC), effectiveness (πCMC), maximum surface excess (Γmax) and minimum surface area (Amin) was determined.

2.2.3 Application as anticorrosion Agents:

Weight loss method:

We used specimens made of carbon steel that measured (3, 1.5, 0.5 cm). To achieve smoothness, the samples were physically polished with fine grade emery paper. Next, rust and oil were removed with acetone, followed by a washing in distilled water, drying, and finally, precise weighing were calculated.

The samples were soaked in 100 ml test solution glass bottles containing 1.0 M HCL with and without the addition of various concentrations of produced surfactants

(5×10-5, 1×10-4, 5×10-4, 1×10-3, 5×10-3, 10×10-3) M where the needed immersion time is around 5 hours.

Following this time, the carbon steel specimen was taken out, cleaned with distilled water, dried, and then weighed where the weight variation was noted.

The following equation gives the weight loss (W) [17]:

$\Delta W = (W1 - W2)$

W1 and W2 represent to the weight of the soaked specimen prior to and following the reaction, respectively. The following equation was used to determine the inhibition efficiency (IE%) [17]:

$IE\ \% = [(\Delta W_{blank} - \Delta W_{inh}) / \Delta W_{blank}] \times 100$

where, respectively, Winh and Wblank express the weight loss of the specimens in the presence and absence of the produced inhibitor.

III. RESULTS AND DISCUSSION

The prepared Gemini non-ionic surfactants made from stearic acid were converted to PEG mono stearate through esterification with polyethylene glycol 400. Di bromo ethane was used to combine these esters to create Gemini non-ionic surfactants (GSC18). Utilizing spectroscopy equipment, the structure of the manufactured Gemini non-ionic surfactant has been elucidated.

3.1. Surface characteristics:

3.1.1. Surface tension:

By evaluating their surface tension at various concentrations, synthetic surfactants can be assessed for their surface-active characteristics. The relationship between logarithmic surfactant concentration and surface tension at 298 K is seen in Fig. 3.

It was discovered that the surfactant solution's surface tension was lower than that of 100% pure bi-distilled water.

3.1.2. Critical micelle concentration (CMC):

Surface tension and the logarithm of surfactant concentration can be utilised for calculating the CMC. Low CMC value was noticed by GS stearate, as may be observed because of the hydrophobic chains having more methylene groups, which causes more repulsion between the molecules of the surfactant [18].

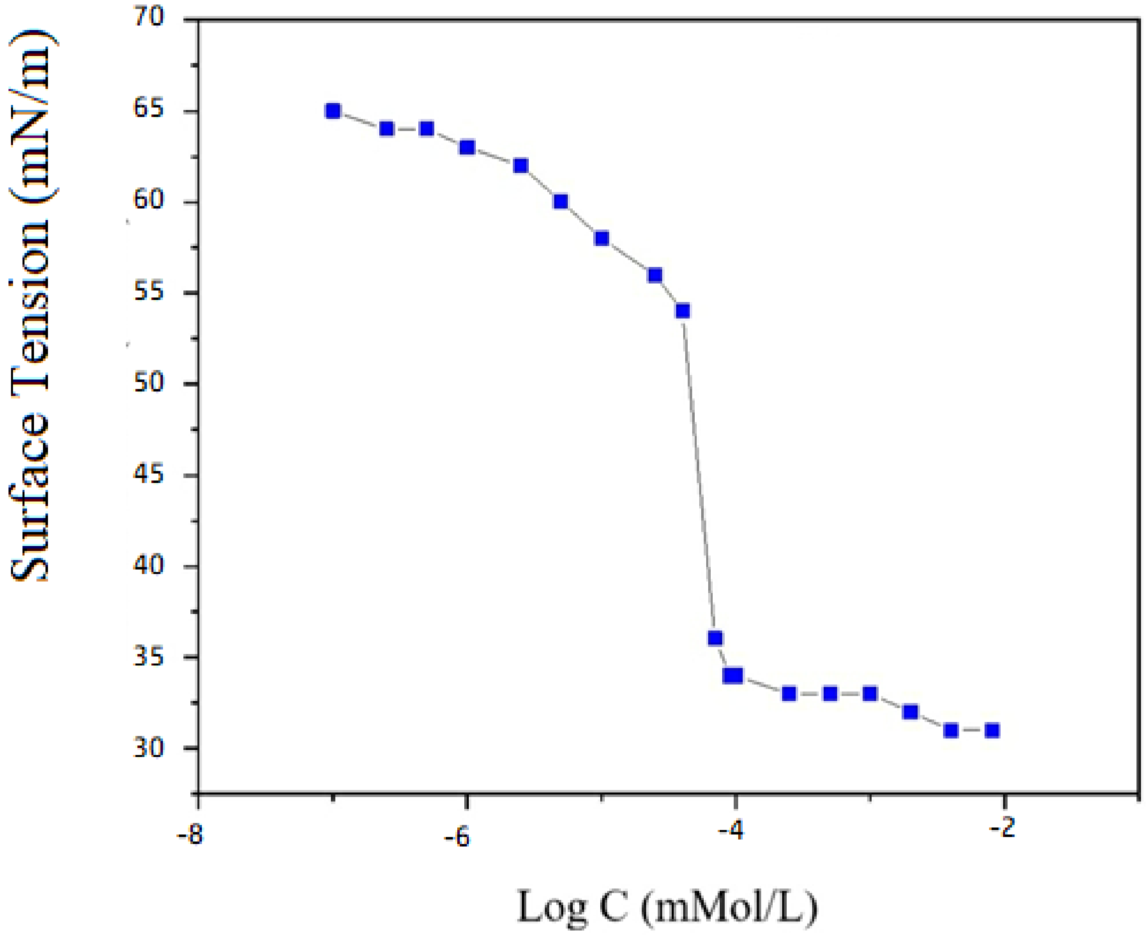

Figure 3: Relation between surface tension and log C of the prepared Gemini non-ionic surfactants at at 298 K.

3.1.3. Effectiveness (π_{cmc}):

Effectiveness was defined and quantified by equation as surface tension reduction by generated surfactant between water that is bidistilled and critical micelle concentration [19].

$$\pi_{cmc} = \gamma_o - \gamma_{cmc}$$

Here, γo is the bi-distilled water's surface tension (71.8 mN/m), and γcmc is the surfactant solution's surface tension at the CMC. The effectiveness calculation revealed that GS stearate has a high effectiveness value.

3.1.4 The Excess of the Surface (Γmax):

Based on the quantity of surfactant adsorption at the air/water interface, the surface excess (Γmax) was calculated. The maximum concentration was determined using the Gibbs adsorption equation [19].

$\Gamma max = (-1/RT)\ (d\gamma/\ d\ lnC)$

Where R is gas constant, T is absolute temperature, (dγ/d lnC) is the slope of the linear line on the surface tension graph. From the Gibbs adsorption equation, Γmax is calculated and the data are shown in table (2)

3.1.5 The Surface Area per Molecule (A_{min}):

Amin, or the amount of space one molecule takes up at the liquid/air interface in units of nm2, is the minimum surface area required by adsorbed molecules. It was calculated using the equation below [20].

$$A_{min} = 10^{14} / N_A\ \Gamma_{max}$$

Where NA is the Avogadro's number. Utilizing this equation, the value of Amin was calculated.

Table (1): Gemini nonionic surfactants surface characteristics:

Surfactant	**CMC x 10-3 (M/L)**	**γc (mN m^{-1})**	**π_{cmc} (mN m^{-1})**	**Γ_{max} (Mol cm^{-2})**	**Amin (nm^2)**
GS stearate	**0.0563**	**33**	**39**	**4.76**	**0.349**

3.2. Corrosion studies:

3.2.1. Weight loss measurements:

The results of the calculations for weight loss, corrosion rate values, and inhibition efficiency (IE%) for carbon steel are presented in Tables.

The data in table (2) shows that the corrosion rate values reduced as the inhibitor concentrations raised in a corresponding order.

The carbon steel surface's inhibitor adsorption and coverage contributed to this behaviour. By blocking the corrosion sites, this adsorption reduces the surface dissolution of carbon steel, thereby reducing weight loss and increasing efficiency as inhibitor concentration increases

Table (2) Corrosion rate of carbon steel, surface coverage and percentage inhibition efficiency for carbon steel in 1.0 M HCL without and with different concentrations of prepared inhibitor.

Conc.	Wt loss. (mg)	Time. (h)	Area. (cm^2)	K. $mg.cm^{-2}h^{-1}$	θ	η %
blank	17.2	5	13.5	0.2548	0.00000	0.0000
5 × 10-5	12.811	5	13.5	0.1898	0.2555	25.5
1 × 10-4	11.603	5	13.5	0.1719	0.325	32.5
5 × 10-4	5.572	5	13.5	0.082	0.676	67.6
1 × 10-3	3.766	5	13.5	0.0558	0.781	78.1
5 × 10-3	1.874	5	13.5	0.02777	0.891	89.1
10× 10-3	1.066	5	13.5	0.0157	0.938	93.8

V –CONCLUION

The prepared Gemini non-ionic surfactants (GSC18) showed promising surface-active characteristics, including low surface tension and a low critical micelle concentration (CMC). The effectiveness and surface excess measurements further demonstrated the quality of the surfactant. Additionally, corrosion studies revealed that the inhibitor concentrations led to reduced corrosion rates and increased inhibition efficiency for carbon steel in 1.0 M HCL. These findings suggest the potential practical applications of the synthesized surfactants in various industrial and commercial settings.

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